

FUNDAMENTAL STUDIES OF VARIOUS POLY(L-LACTIDE)/CLAY
NANOCOMPOSITE SYSTEMS BY IN-SITU
POLYMERIZATION

THESIS

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To Meghan

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ABSTRACT

FUNDAMENTAL STUDIES OF VARIOUS POLY(L-LACTIDE)/CLAY NANOCOMPOSITE SYSTEMS BY IN-SITU POLYMERIZATION

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Texas State University-San Marcos

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SUPERVISING PROFESSOR GARY W BEALL

Biodegradable plastics are a promising solution to the increasing global concern of persistent plastic wastes on the environment. In order for biodegradable polymers to successfully compete with commodity polymers, mechanical, thermal, and gas barrier properties must be improved. This can be achieved by dispersing inorganic fillers into the polymer matrix, thus forming an exfoliated polymer nanocomposite. In this study, *in situ* polymerizations of poly(L-lactide)-clay nanocomposites were conducted using various montmorillonite organoclays (PLLA-MMT). When using tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) as the catalyst, the reaction is believed to initiate from stannous alkoxides, formed from hydroxide ($-\text{OH}$) groups present in the reagents. Several quaternary ammoniums were ion-exchanged onto the surface of montmorillonite-

Na^+ in order to test effects on the color, morphology, and molecular weights of the final composites. Final products were characterized by Gel Permeation Chromatography (GPC), X-ray diffraction (XRD), and Thermal Gravimetric Analysis (TGA). Exhaustive purification of all reagents, especially monomer, proved to be essential for the polymerization of high molecular weight poly(L-lactide) ($M_w > 10^5$). Ultrasonic agitation in toluene was found to be the best technique for dispersing organoclays prior to polymerization. The effects of catalyst concentration, clay loading, and reaction time on PLLA-MMTs were determined. For PLLA-nanocomposites, molecular weight decreased as the clay loading increased. There was also a slight correlation found between catalyst concentration and molecular weight. It was confirmed that the optimal $[\text{monomer}]_0/[\text{Sn}]$ molar ratio for pristine PLLA (180°C, 8 h) is 40,000, while for PLLA-MMT is ~ 45 times as concentrated. XRD analysis revealed several exfoliated nanocomposites. Excessive washing of organoclays for removal of Na^+ , silane edge treatment, and addition of a linking agent did not significantly improve molecular weight of PLLA-MMT.

CHAPTER 1

INTRODUCTION

1.1 Background

The twentieth century marked a time in which thermoplastic polymers began dominating the industrial world in virtually all applications. An increase in polymer production was soon accompanied by an increase in volume of plastic refuse. The total amount of plastics in municipal solid wastes (MSW) was 26.7 million tons, representing 11.1 percent of total MSW generation in 2003.¹ The vast majority of domestic and commercial waste is put into landfills, because direct costs are substantially lower than disposal by other means. The environmental impact of persistent plastic wastes is an increasing global concern. Also, since the raw material for conventional plastics is finite and derived directly from the petroleum industry, the increasing costs of fossil fuels will cause the cost of production of conventional plastics to climb. For these reasons, there is an urgent necessity to develop renewable, bio-friendly plastic materials.

1.2 Poly(L-lactide): Biofriendly Thermoplastic

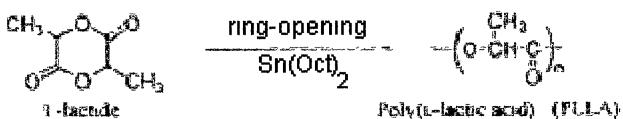
Researchers have found poly(L-lactide) (PLLA) attractive since it is produced from renewable resources (e.g., corn) and is readily biodegradable. PLLA is a linear

aliphatic thermoplastic polyester that is broken down into CO₂ and H₂O by microorganisms in high temperature and humid environments. This polymer can fully degrade in about two months in commercial composts at 60°C and 80% relative humidity.²

Unfortunately, the mechanical and thermal properties of PLLA must be improved so that this polymer can compete with conventional plastics. In this research, inorganic fillers were added as reinforcement to the polymer in an attempt to improve these properties. This will be discussed in greater detail later.

1.2.1 PLLA Synthesis: From Corn to Plastic

PLLA is produced by first milling, then cooking a renewable resource (e.g., corn) for 30 to 40 hours at 50°C. This process separates starch from the raw material. D-glucose or dextrose, in turn, is processed from the starch. Microorganisms ferment the unrefined dextrose into lactic acid through a fermentation process similar to that used by beer producers. Water is removed in order to concentrate the lactic acid, which is then polymerized by further evaporation to form low molecular weight poly(lactic acid) molecules. The short poly(lactic acid) molecules are depolymerized in the presence of a catalyst into lactide dimers. The crude lactide generated is distilled to remove water and other impurities. The lactide can finally be polymerized via ring-opening using the covalent metal carboxylate, tin(II) octoate (tin(II) 2-ethylhexanoate (Sn(Oct)₂)) into PLLA (eq 1).³



Equation 1. Schematic Representation of the Ring-opening Polymerization of L-lactide into PLLA.

A mechanism has been proposed by several groups,⁴⁻⁷ in which Sn(Oct)₂ reacts with compounds containing hydroxide (-OH) groups and results in the formation of tin(II) alkoxide or hydroxide initiators. The polyester chain is assumed to propagate via monomer insertion on the tin(II) alkoxide as the active center. In 2000, Kowalski et al. observed active species, i.e., Sn(II)-containing species, incorporated at the end groups in one population of macromolecules from MALDI-TOF experiments, supporting this mechanism.⁸ Also, kinetic studies of cyclic esters initiated with tin(II) octoate suggested that polymerization proceeds on the tin(II)-alkoxide bond.⁹

1.2.2 Competition with Commodity Plastics

PLLA is a promising polymer that is currently being used for consumer goods, food packaging, and serviceware by NatureWorks® LLC. However, in order to compete with commodity plastics, the flexural properties, heat distortion temperature (HDT), and gas permeability of PLLA must be enhanced.¹⁰

HDT is an important quantity because it signifies the temperature at which the polymer begins to distort or deflect under a given load. The distortion temperature under load (DTUL) of PLLA at 1.8 MPa is approximately 66°C. A typical petroleum-based plastic, acrylonitrile butadiene styrene (ABS), has a DTUL of 90°C under the same

conditions.¹¹ By increasing the HDT of PLLA, the biofriendly plastic could replace conventional polymers in durable applications like automotive and computers.

Polyethylene terephthalate (PET) is a widely used thermoplastic polymer for packaging applications. PLLA has gas permeability values higher than the petroleum-based PET. For example, PLLA and PET have O₂ permeabilities of 1.21 and 0.76, respectively (10^{-10} g m/m² s bar).^{12,13} Slowing the permeability of gas molecules (e.g. O₂) through a plastic container can significantly extend the shelf life of food.

Extensive research has been performed aiming to improve the properties of PLLA in order to compete with low cost, flexible commodity polymers. Research has focused on the blending of PLLA with other additives in order to improve the HDT of the polymer composite. Some groups have melt compounded PLLA with ultrafine inorganic particles like talc leading to nucleating effects where crystallization is observed. This process led to an essentially intercalated nanocomposite.¹⁴⁻¹⁶ Other researchers have attempted to synthesize the PLLA chains *in situ* from initiators located on the surface of the clay.¹⁷ This technique is more likely to result in an exfoliated nanocomposite. For our purposes, the latter method was employed.

1.3 Smectite Clays: Background and Structure

Smectite clays such as montmorillonite (MMT) can be synthesized or more commonly refined from naturally occurring bentonite. The morphology of montmorillonite can be viewed in the scanning electron microscope (SEM) image in Figure 1.

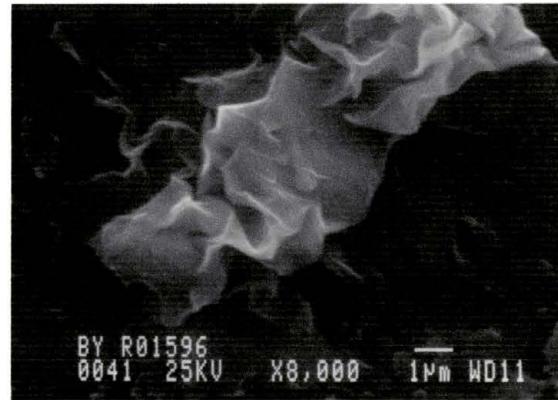


Figure 1. SEM Image of Montmorillonite Clay. Scale bar 1 micron.

In 1931, Hoffman et al. began a study of smectite which resulted in a suggested structure for this mineral which is now widely accepted in its broader form.¹⁸ The structure of smectite is illustrated below in Figure 2.

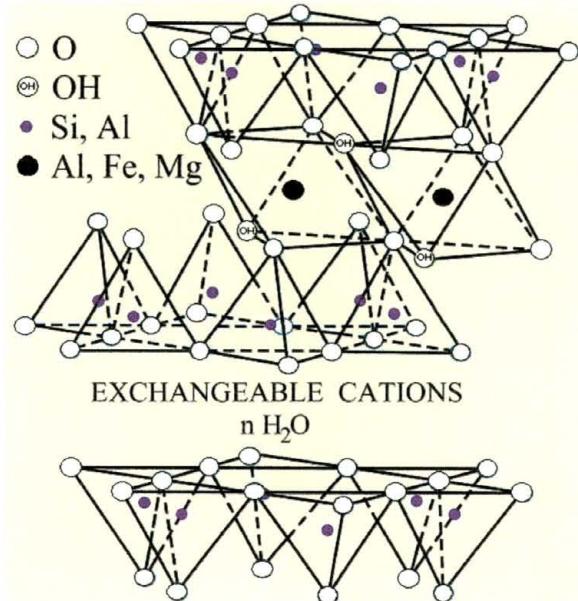


Figure 2. Diagrammatic Sketch of the Structure of Smectite.¹⁹

Montmorillonites are 2:1 layered structures consisting of a central octahedral Al sheet sandwiched between two tetrahedral Si sheets via oxide anions. Isomorphic substitution of Mg^{2+} for Al^{3+} in the octahedral sheet causes an excess of negative charges within the montmorillonite layers. These negative charges are most often counterbalanced by free-moving (exchangeable) cations like Na^+ and sometimes Ca^{2+} . Water molecules are typically found associated between the clay layers because of the hydrophilicity of the cations. The edges of the crystal are usually terminated in hydroxyl groups. Smectite clays are assigned cation exchange capacities (CEC) which are conventionally given in units of milliequivalents/100g clay. These values can vary based on clay type and geographical location. Montmorillonite is a type of phlo-silicate that is composed of stacks of individual sheets with dimensions of 1 nm thickness and lengths of approximately 220 nm.²⁰

1.4 Polymer-clay Nanocomposites

A true nanocomposite is formed only when clay nanolayers are uniformly dispersed (exfoliated) in a polymer matrix (Figure 3C and D), as opposed to being aggregated as tactoids (Figure 3A) or merely intercalated (Figure 3B).

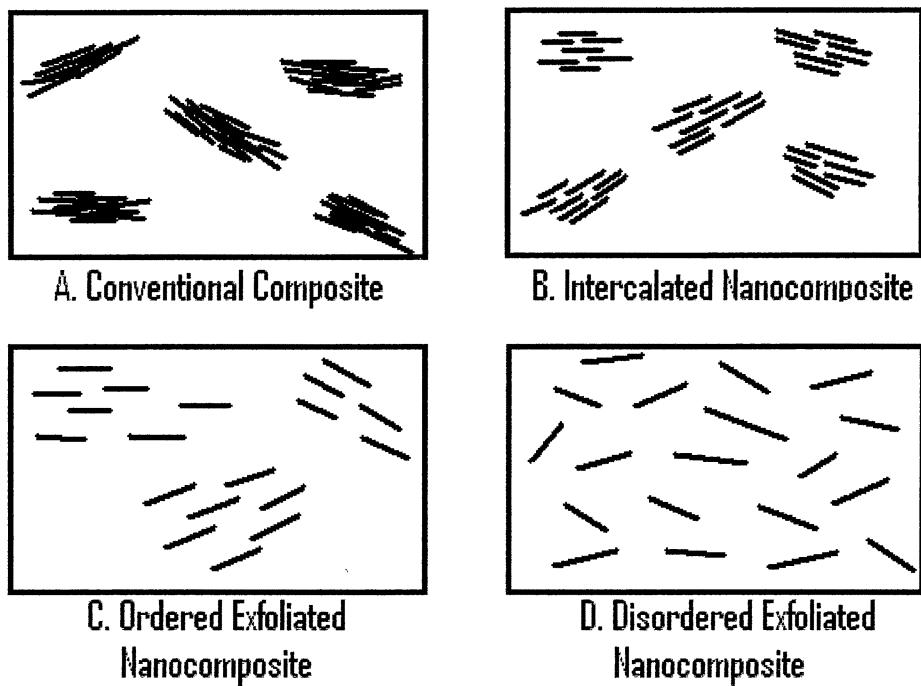


Figure 3. Schematic Representation of (A) a Conventional, (B) an Intercalated, (C) an Ordered Exfoliated, and (D) a Disordered Exfoliated Polymer-clay Nanocomposite.

The spacing between clay plates (i.e., basal d-spacing) is fixed in an intercalated nanocomposite, whereas, the interlayer spacing in exfoliated nanocomposites varies based on clay loading.

1.4.1 Property Enhancement of Nanocomposites

In the last few decades, nanocomposites have become a very popular area of research.²¹⁻²⁵ Exfoliated nanocomposites are attractive to researchers since they often exhibit improved mechanical, thermal, and gas barrier properties, even at low filler content (as low as 1 wt.-%) in comparison to conventional (micro)-composites (>30 wt.-% of microfiller).²⁶ When nanolayers are truly dispersed in a polymer, the number of

reinforcing components is optimized for carrying an applied load and deflecting cracks. The high surface area of clay ($\sim 750 \text{ m}^2/\text{g}$) in contact with polymer aids in stress transfer to the reinforcement phase, enabling mechanical property enhancement. The high aspect ratio (platelet length to thickness ~ 1000) of the impermeable clay layers gives rise to a tortuous pathway a molecule must maneuver around in order to permeate the nanocomposite.²⁷ This highly debated model is shown in Figure 4.

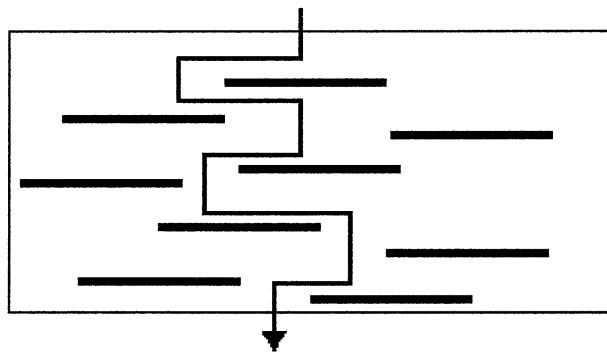


Figure 4. Proposed Tortuous Path Model of Permeant Through a Polymer-clay Nanocomposite.²³

Even at low clay loadings, strength and modulus could be significantly increased, and gas permeability rate could be reduced.²⁸⁻³⁰

1.4.2 Obstacles to Property Enhancement of Nanocomposites

Clay plates typically agglomerate as tactoids in a polymer medium due to their preferred face-to-face stacking, giving rise to a poor dispersion. In this state, rigidity is typically improved at the cost of strength, toughness, and elongation. Another factor which impedes the dispersion of clay plates into individual monolayers is the inherent incompatibility of the hydrophilic layered silicates with the hydrophobic polymer matrix.

However, in the late 1980's, researchers at Toyota demonstrated that layered silicates could be tailored to be compatible with the polymer matrix by exchanging the inorganic cations from the clay galleries with alkylammonium surfactants.³¹ In the early 1990's, a group successfully polymerized a nylon 6-clay nanocomposite from the gallery of an organoclay.^{32,33} At a clay loading of only 4.2 wt.-%, the tensile modulus doubled, the tensile strength increased more than 50%, and the heat distortion temperature increased by 80°C compared to the pristine polymer.³⁴⁻³⁶ Exchanging the cations with organic onium ions also assists in expanding the clay galleries if the polarities of the organoclay and monomer are similar. For example, the unreacted precursors, ϵ -caprolactam,³² epoxides,³⁷ and polyols,³⁸ were observed to intercalate organoclay galleries.

1.5 The Scope of this Research

In this study, various commercially available organically modified layered silicates (OMLS) were compared in order to investigate their influences on the polymerization of L-lactide to poly(L-lactide). Also, sodium from Cloisite® Na⁺, i.e., natural montmorillonite-Na⁺, was ion exchanged with a range of different alkylammonium surfactants in order to test the effects of other organoclays on color, thermal properties, intercalation, and molecular weight of PLLA-nanocomposites.

In these experiments, the hydroxyl groups, which are projected to initiate the polymerization (Section 1.2.1), are located on the alkyl ammonium cations. Having the initiator inside the clay galleries should provide a driving force for the delamination of the clay in the polymer matrix. The density of the surface hydroxyl groups was controlled in order to achieve a targeted molecular weight by adjusting the ratio of

hydroxyl-terminated and hydroxyl-free alkylammonium surfactants. This should also lower the grafting density or the concentration of polymer chains growing off of the surface, compared to an exchange in which the clay is modified by a 100% -OH surfactant.

Over the course of this study, the degree to which the monomer was purified was enhanced, and the molecular weight of PLLA was compared at different levels of purification. The effects of loading, edge treatment, and excessive washing of organoclays for removal of salts were examined. Polymerization times and catalyst concentrations were optimized.

Several setups were utilized throughout this study. Various solvents and agitation techniques were compared for dispersing organoclays prior to polymerizations. Dimethyl terephthalate was tested as a possible linking agent for low molecular weight chains of PLLA. Finally, the effects of having free alkyl ammonium chains present in the polymerization of PLLA were studied. Molecular weights of the nanocomposites were determined by Gel Permeation Chromatography (GPC). Thermogravimetric analysis (TGA) was used in order to obtain thermal characteristics of the nanocomposites. X-ray diffraction (XRD) was utilized in order to monitor the extent of exfoliation or intercalation of the clay platelets in the polymer matrix.

CHAPTER 2

EXPERIMENTAL

2.1 Materials

Cloisite® Na⁺ (Na⁺-MMT), Cloisite® 10A, Cloisite® 20A, and Cloisite® 30B (from Southern Clay Products (Texas, U.S.A.)) were used as received with no additional purifications. The cation exchange capacity for Cloisite® Na⁺, as provided by the manufacturer, was 92.6 meq/100g clay. Cloisite® 10A had been organically modified with 2MBHT (dimethyl, hydrogenatedtallow, benzyl, quaternary ammonium chloride) at a concentration of 125 meq/100g clay. Cloisite® 20A was previously modified with 2M2HT (dimethyl, dihydrogenatedtallow, quaternary ammonium chloride) at 95 meq/100g clay. Cloisite® 30B had been organically modified with MT2EtOH (methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride) at 90 meq/100g clay.

Ethoquad (MT2EtOH), Arquad (2M2HT), Armosoft DEQ (dimethyl, diesterhydrogenatedtallow, quaternary ammonium chloride), and Armosoft PHT TEQ (methyl, diesterhydrogenatedtallow, 2-hydroxyethyl, quaternary ammonium chloride) were obtained from Akzo Nobel and were used as received. Ethoquad and Arquad were both listed as 85% active. Armosoft DEQ and Armosoft TEQ were listed as 1.1 meq/g and 1.143 meq/g active, respectively. The structures of the alkylammonium surfactants used in this study are shown in Figure 5.

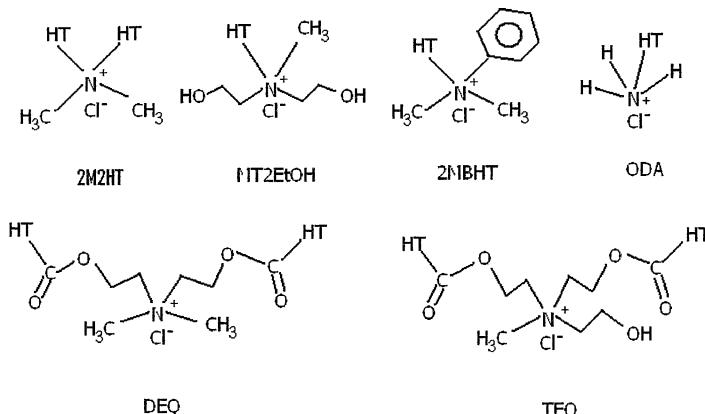


Figure 5. Alkylammonium Surfactants Ion-exchanged Onto the Surface of Montmorillonite.

L-lactide (LLA, from NatureWorks® LLC) was recrystallized in a solution of toluene (VWR, washed with cold H₂SO₄ and distilled from sodium) and tetrahydrofuran (THF) (VWR, distilled from sodium) under argon, washed, and dried under vacuum overnight, then taken directly to the dry box. All glassware used in this procedure was oven-dried at 120°C. Poly(L-lactide) (PLLA, from NatureWorks® LLC) was used as received for molecular weight comparisons.

Tin(II) 2-ethylhexanoate (Sn(Oct)₂, from Aldrich) was vacuum distilled at 140°C in an attempt to remove acidic proton impurities (e.g., 4.5 wt.-% octanoic acid and 0.5 wt.-% H₂O).³⁷ The vacuum required in order to distill off the impurities was not achieved, since only a few drops were collected in the catch flask. A stock solution of Sn(Oct)₂ was prepared in anhydrous toluene.

Other reagents used throughout this study along with the companies which supplied them are listed in Table 1. All reagents were used as received.

Table 1. List of Reagents and Suppliers.

Reagent(s)	Suppliers
Octadecylamine	Sigma
Phenyl triethoxy silane	United Chemical Tech.
Dimethyl terephthalate, benzene, decane, DMSO, phenyl ether	Aldrich
Hexane, pentane, xylene, dichloromethane	VWR
Chloroform (HPLC grade)	EMD Chemicals

2.2 Organoclay Preparation

2.2.1 Dry Method

Cloisite® Na⁺ (250 g, for extrusion purposes) was weighed into a Kichen Aid® Bowl Mixer apparatus. Deionized water was added slowly to the clay while mixing at a slow speed. This was done until the clay was wetted into a gravel-like consistency (i.e., small beads or pellets). By wetting the clay, the galleries begin to swell, becoming more receptive to the introduction of the quaternary salts. The alkylammonium salts were melted in a double boiler with boiling water. The molten salts were then added to the bowl and allowed to mix for a brief period. The amount of each quaternary ammonium was typically controlled to give a theoretical molecular weight between 75,000 g mol⁻¹ to 100,000 g mol⁻¹. It is known that M_w should be more than 70,000 to make use of the sufficient physical properties of PLLA. The semi-wet clay was processed through a model 4522 Hobart Commercial Auger Extruder. The machine provided sufficient heat

and shear in order to facilitate diffusion of the quaternary salts into the clay galleries. The organoclay was processed ~ 3 times through the mini-extruder, until steam was observed escaping from the instrument. At this point the organoclay strands had a sheen-like appearance. After the procedure was completed, the modified clay was washed, pulverized, and finally oven-dried at 70°C until ready for use. In subsequent clay preparations, organoclays were oven-dried overnight at 70°C, pulverized, and then washed in a column of deionized water until AgNO₃ tests were negative to the presence of Cl⁻ ions. This would indicate an absence of salts which could adversely participate in future syntheses. The washed organoclay was again oven-dried at 70°C and finally ground with a mortar and pestle and sieved through a 325 mesh screen to give 45µm clay particles. The finished clay was dried in a vacuum oven at 70°C overnight and taken into the dry box for future use.

2.2.2 Small Scale Method – Silane Edge-treatment

In this method, 2M2HT/MT2EtOH – MMT organoclay was wetted with anhydrous toluene in a mortar. Phenyl triethoxy silane was added at 3.6 wt.-% to the organoclay. The mixture was sheared with a pestle for a brief period. The final product was dried in an oven at 70°C and pulverized to a particle size of 45 µm.

2.2.3 Wet Method - Preparation of ODA/TEQ – Modified MMT

Only in the case of octadecylamine was a wet method employed in order to prepare the quaternary ammonium salt. One mole octadecylamine was acidified into octadecylammonium by one mole of concentrated HCl in a solution of deionized water at

80°C. Armosoft PHT TEQ was added in the amount necessary to give a target molecular weight of approximately 100,000 g mol⁻¹. The solution was added to ~ 1 % montmorillonite dispersion in water. The clay solution was agitated in a D-51580 Reichshof Dispermat® at 3000 – 4000 rpm for 30 minutes.

2.3 Organoclays Prepared for Polymerization of PLLA-MMT

All of the organoclays that were prepared for this study are listed in Table 2.

Table 2. List of Organoclays Prepared for Polymerization in the Order Used.

Organoclay (Modifier(s))	Modifier(s) Concentration	Comments
(1) 2M2HT/MT2EtOH*	82.3 meq 2M2HT/100g clay 12.7 meq MT2EtOH/100g clay	Used for the majority of study Designed for 5 % clay loaded PLLA at 75,000 g mol ⁻¹
(2) 2M2HT/MT2EtOH*	82.3 meq 2M2HT/100g clay 12.7 meq MT2EtOH/100g clay	Excessive washing AgNO ₃ test for Cl ⁻ performed
(3) 2M2HT/MT2EtOH*	82.3 meq 2M2HT/100g clay 12.7 meq MT2EtOH/100g clay	Small scale (mortar & pestle) used for silane treatment 3.6 wt.-% phenyl triethoxy silane added to organoclay (2)
(4) 2M2HT/MT2EtOH*	85.5 meq 2M2HT/100g clay 9.5 meq MT2EtOH/100g clay	5.0 wt.-% phenyl triethoxy silane added Designed for 5 % clay loaded PLLA at 100,000 g mol ⁻¹
(5) 2M2HT/MT2EtOH*	85.5 meq 2M2HT/100g clay 9.5 meq MT2EtOH/100g clay	2.5 wt.-% phenyl triethoxy silane added Designed for 5 % clay loaded PLLA at 100,000 g mol ⁻¹
(6) TEQ*	95 meq TEQ/100g clay	
(7) ODA*	95 meq ODA/100g clay	
(8) DEQ*	95 meq DEQ/100g clay	
(9) ODA/TEQ*	76 meq ODA/100g clay 19 meq TEQ/100g clay	For 5 % clay loaded PLLA at 100,000 g mol ⁻¹

* See Section 2.1 for structures.

2.4 Dispersing Organoclay in a Solvent

Various solvents were tested as possible media for the dispersal of modified-MMT. Pentane, hexane, decane, benzene, toluene, xylene, diphenylether, dichloromethane, chloroform, water, THF, and DMSO were studied as possible dispersing agents for organoclay (1) (see Table 2). The effects of heat, shaking, agitation via Dispermat®, and ultrasonic agitation were compared as agitation methods for dispersing organoclays. The upper limit of clay loading with respect to solvent was also determined. Above this concentration, gels would form which would render them too viscous for ultrasonic agitation. Polymerizations discussed later in the text will utilize a 10 minute period of ultrasonic agitation (20 kHz, 100W) via a Model 501 High Intensity Ultrasonic Processor by Sonics & Materials.

2.5 *In situ* Polymerization

Initially bulk polymerizations were conducted in small vials (20 ml). 5 g L-lactide was added to an organoclay suspension. Only in the case of a few preliminary reactions, polymerizations were conducted with dry clay to test the effect of not having a solvent present on the homogeneity of the final product. Finally, Sn(Oct)₂ was added to the vial at a monomer to catalyst ratio ~ 350, although this concentration was varied in order to test the effects of different catalyst concentrations on the polymerization. The mixture was heated to 180°C for 8 hrs. Argon was bubbled into the reaction via pipette while stirring and evaporating off solvent. The experiments conducted in vials served to give a fundamental understanding of the dispersion and polymerization process.

The *in situ* polymerization process was later performed in 250 ml three-necked flasks accompanied with a mechanical stirrer and a firestone valve which allowed for a facile switch between vacuum and argon. The flask was connected to a condenser which drained into a catch flask for the collection of solvent as the reaction temperature increased to 180°C. Starting material in this set-up ranged from 40 – 50 g of L-lactide monomer; purified as described in Section 2.1 (one rinse). In these experiments, Sn(Oct)₂ was added to the reaction vessel at a monomer to catalyst ratio ~ 800.

In order to recover the final product, the reaction vessel was quenched in a dry ice/acetone bath which would typically break the glass free from the product. Because of this, the three-necked flask set up was replaced with a large test tube connected to another test tube with a sidearm via a bent glass rod which served as a condenser for the reaction as shown in Figure 6.

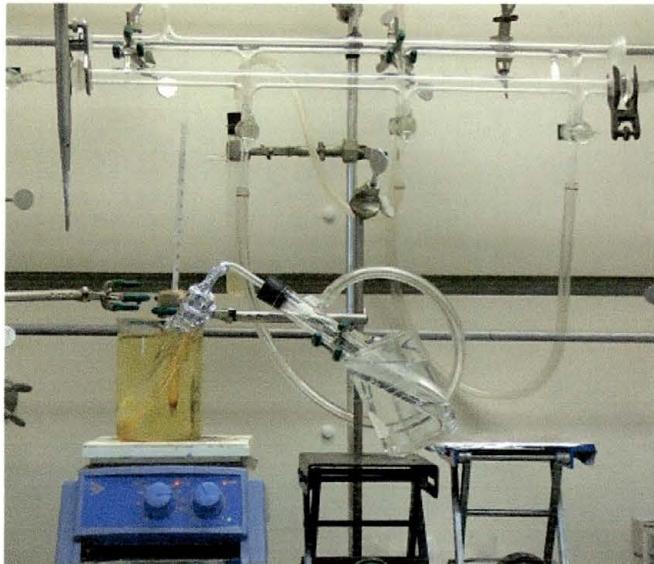


Figure 6. Reaction Setup for *In Situ* Polymerization of PLLA-nanocomposite.

Argon was fed through the side arm of the catch tube. A magnetic stir bar was used for mixing the reagents and also aided in observing viscosity changes indicating increase in molecular weight. In this setup, 5 – 10 g samples of purified L-lactide (two rinses) were used as starting material. Also, Sn(Oct)₂ was added to the reaction vessel at a monomer to catalyst ratio ~ 889 – 1000.

2.6 Various Nanocomposites Synthesized

Table 3 is an exhaustive record of the reactions which were performed in this study.

Table 3. List of Polymerizations Conducted in Chronological Order.

Polymer/ Nanocomposite	Reaction Conditions	Comments
1) 0, 1, 5, 10 % organoclay (1) in PLLA (several runs)	180°C, 8 h, monomer: catalyst ~ 350 (5 g L-lactide) ^{p1}	Some polymerizations used toluene as a dispersing agent for the clay (after this, all future polymerizations were done in toluene)
2) 5 % organoclay (1) in PLLA	180°C, 8 h, monomer: catalyst ~ varied (5 g L-lactide) ^{p1}	Catalyst concentrations effects studied at 40,000: 1, 4,000: 1, 1600: 1, and 800: 1 monomer: catalyst
3) Pristine PLLA	180°C, 8 h, monomer: catalyst ~ varied (5 g L-lactide) ^{p1}	Catalyst concentrations effects studied at 40,000: 1, 4,000: 1, 1600: 1, and 800: 1 monomer: catalyst
4) 4.28 % organoclay (1) in PLLA	180°C, 8 h, monomer: catalyst ~ varied (5 g L-lactide) ^{p1}	Catalyst concentrations effects studied at 40,000: 1, 4,000: 1, 1600: 1, and 800: 1 monomer: catalyst
5) 4.28 % organoclay (1) in PLLA	180°C, 8 h, monomer: catalyst ~ 800 (40 g L-lactide) ^{p1}	
6) 3 % organoclay (1)	180°C, 8 h, monomer: catalyst ~ 800 (50 g L-lactide) ^{p1}	
7) Pristine PLLA	180°C, 8 h,	

	monomer: catalyst ~ 800 (50 g L-lactide) ^{p1}	
8) Pristine PLLA	180°C, 2 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p2}	
9) Pristine PLLA	180°C, 4 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p2}	
10) Pristine PLLA	180°C, 6 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p2}	
11) Pristine PLLA	180°C, 8 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p2}	
12) Pristine PLLA	180°C, 10 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p2}	
13) Pristine PLLA	180°C, 8 h, monomer: catalyst ~ 40,000 (5 g L-lactide) ^{p1}	
14) 3 % organoclay (1)	180°C, 8 h, monomer: catalyst ~ varied (5 g L-lactide) ^{p2}	Catalyst concentrations effects studied at 40,000: 1, 4,000: 1, 2000: 1, 1333: 1, 1000: 1, and 800: 1 monomer: catalyst
15) 1, 2, 3, 4, 5 % organoclay (1) in PLLA	180°C, 8 h, monomer: catalyst ~ 1,000 (5 g L-lactide) ^{p2}	
16) 1 % organoclay (2)	180°C, 8 h, monomer: catalyst ~ 1,000 (10 g L-lactide) ^{p2}	
17) 5 % organoclay (2)	180°C, 8 h, monomer: catalyst ~ 1,000 (5 g L-lactide) ^{p2}	
18) 4 % organoclay (3)	180°C, 8 h, monomer: catalyst ~ 1,000 (5 g L-lactide) ^{p2}	
19) 4 % organoclay (2) (Dimethyl terephthalate added to aliquot ½ h prior to termination)	180°C, 8 h, monomer: catalyst ~ 1,000 (5 g L-lactide) ^{p2}	
20) 4 % organoclay (2)	180°C, 8 h, monomer: catalyst ~ 1,000 (5 g L-lactide) ^{p2}	
21) Pristine PLLA	180°C, 8 h, monomer: catalyst ~ 1,000	High catalyst concentration probably not necessary for

	$(5 \text{ g L-lactide})^{p^2}$	pristine reaction
22) Pristine PLLA (NO ultrasonic agitation performed)	180°C, 8 h, monomer: catalyst ~ 1,000 $(5 \text{ g L-lactide})^{p^2}$	High catalyst concentration probably not necessary for pristine reaction
23) Pristine PLLA	180°C, 8 h, monomer: catalyst ~ 1,000 $(5 \text{ g L-lactide})^{p^2+}$	High catalyst concentration probably not necessary for pristine reaction
24) 5 % organoclay (2)	180°C, 8 h, monomer: catalyst ~ 1,000 $(5 \text{ g L-lactide})^{p^2+}$	
25) 5 % Cloisite® 20A in PLLA	180°C, 8 h, monomer: catalyst ~ 1,000 $(5 \text{ g L-lactide})^{p^2+}$	Lacked (-OH) groups on clay
26) 5 % organoclay (4)	180°C, 8 h, monomer: catalyst ~ 1,000 $(5 \text{ g L-lactide})^{p^2+}$	
27) 5 % organoclay (5)	180°C, 8 h, monomer: catalyst ~ 889 $(5 \text{ g L-lactide})^{p^2+}$	
28) PLLA with free quaternary ammoniums (no clay)	180°C, 8 h, monomer: catalyst ~ 889 $(5 \text{ g L-lactide})^{p^2+}$	Amount that would be present on 5 % organoclay To test the effects of quaternary ammonium salts on the degradation or color change of product
29) 1 % Cloisite® 30B in PLLA	180°C, 8 h, monomer: catalyst ~ 889 $(5 \text{ g L-lactide})^{p^2+}$	Became viscous in less than 1 h High catalyst concentration probably not required for this reaction 8 h may have been too long for this catalyst concentration because the nanocomposite began slowly darkening much like it does in pristine PLLA when excess cat. conc. is used and the reaction time is held constant.
30) 1 % organoclay (6) in PLLA	180°C, 8 h, monomer: catalyst ~ 889 $(5 \text{ g L-lactide})^{p^2+}$	Viscous at t ~ 0 h High catalyst concentration probably not necessary for pristine reaction
31) 5 % organoclay (7) in PLLA	180°C, 8 h, monomer: catalyst ~ 889 $(5 \text{ g L-lactide})^{p^2+}$	Initially good color, low viscosity Viscous at t ~ 3.5 h

32) 5 % Cloisite® 10A in PLLA	180°C, 8 h, monomer: catalyst ~ 889 (5 g L-lactide) ^{p2+}	Initially good color, low viscosity Significant darkening over course of polymerization
33) 5 % organoclay (8) in PLLA	180°C, 8 h, monomer: catalyst ~ 889 (5 g L-lactide) ^{p2+}	Initially good color, low viscosity Clay did not disperse well in toluene upon ultrasonic agitation Darkened over course of polymerization Viscosity slightly increased over course of reaction
34) 5 % organoclay (9) in PLLA	180°C, 2 h, monomer: catalyst ~ 889 (5 g L-lactide) ^{p2+}	Initially good color, highly viscous material High catalyst concentration probably not necessary for pristine reaction (color slightly darkened over time)
35) 5 % organoclay (9) in PLLA	180°C, 8 h, monomer: catalyst ~ 889 (5 g L-lactide) ^{p2+}	Initially good color, highly viscous material High catalyst concentration probably not required for pristine reaction (color slightly darkened over time)

i monomer used as received with no purification.

p1 monomer recrystallized with 1 wash.

p2 monomer recrystallized with 2 washes.

p2+ monomer recrystallized with 2 washes; all reagents dried/purified to our limits; stored in dry box.

2.7 Characterization of Monomer and Nanocomposites

2.7.1 Determination of Melting Points

The purified L-lactide had a melting point ranging from 100.6 – 102.4°C, while the as-received L-lactide had a melting point range of 95.1 – 96.8°C. A MEL-TEMP II melting point apparatus was used to collect these data.

2.7.2 Determination of Molecular Weight

Molecular weights of PLLA-nanocomposites were determined via gel permeation chromatography (GPC). All products (25 mg) were dissolved in 5 ml HPLC grade chloroform (CHCl_3) and subsequently filtered through a 0.45 μm Teflon filter. The filtered solution (50 μl) was injected and eluted through a series of columns consisting of two Waters Styragel[®] HR 4E columns, a Styragel[®] HR 5E column, and a Polymer Laboratories PLgel 5 μm , 50 \AA column at 1 ml min^{-1} with HPLC-grade CHCl_3 as the mobile phase over a period of 60 minutes. Molecular weights and molecular distributions were calculated by reference to a universal calibration curve relative to polystyrene (PS) standards. Commercial PLLA from NatureWorks[®] LLC was tested for comparison. A Waters 600E Multisolvent Delivery System was used for this study. Polymer fractions were detected via a Waters 2410 differential refractometer.

2.7.3 Determination of Thermal Stability

Thermogravimetric Analysis (TGA) was performed in order to determine the thermal stability or the temperature of decomposition of various organoclays and nanocomposites described in the previous section. Sample mass was monitored in a platinum pan by means of a thermobalance and the temperature was increased from room temperature to 800°C on a 20°C/min temperature ramp in an inert (i.e., argon) atmosphere. Data were recorded as a thermogram of weight % versus temperature. By performing a first derivative operation on the mass loss curve, significant changes in sample mass with respect to temperature may be observed. Weight loss from evaporation of water in the clay gallery is typical at $\sim 100^\circ\text{C}$. At higher temperatures weight loss

results from polymer decomposition. TGA scans were performed on a TA Instruments, Inc. TGA Q50.

2.7.4 Determination of Degree of Exfoliation / Intercalation

X-ray diffraction (XRD) studies were performed on nanocomposite samples in order to see if clay plates were intercalated or exfoliated in the polymer matrix. By comparing peak intensities, the degree of intercalation could be predicted. When no peak was present in a scan, the sample was projected to be exfoliated. All X-ray patterns were measured using a Bruker AXS D8 Focus X-ray diffractometer. Radial scans versus scattering angle (2θ) (Figure 7) were recorded at room temperature in the range of $1 - 22^\circ$ (2θ) (step size = $0.02^\circ(2\theta)$, scanning rate = 2 s/step) with identical settings of the instrument by using filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), an operating voltage of 35 kV, and a filament current of 35 mA. XRD studies were carried out on samples melted onto glass slides.

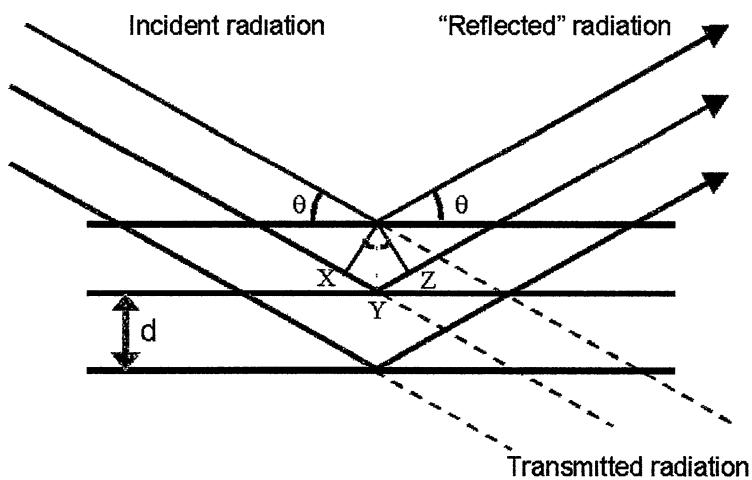


Figure 7. Diagram of X-ray Scattering Angle (2θ).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 The Synthesis of a PLLA-nanocomposite

Due to the large number of methods and variations of the synthesis, the results and discussion will be presented chronologically in the order they were conducted.

3.2 Polymerization of PLLA/ PLLA-nanocomposite

3.2.1 Polymerization in Vials

In the preliminary experiments, Sn(Oct)₂ catalyst was added as received (monomer to catalyst ratio ~ 350) to a 5 wt.-% 2M2HT/MT2EtOH-modified-MMT in as received L-lactide. The organoclay precipitated out of the polymer. Samples were also exposed to air causing the product to become oxidized which could be observed by darkening of the sample. The nature of the decomposed product (dark color) has not yet been determined. This experiment made clear the importance of finding a suitable solvent to aid in the dispersion of the clay into the final product. Also, the decision to purge the reaction with argon was determined from these reactions.

3.2.2 The Search for the Proper Solvent

After testing the solvents listed in Section 2.4, it was determined that toluene was the most effective solvent for dispersing the organoclays used in this project. This decision was made by weighing a controlled amount of organoclay into each of the solvents and ultrasonically agitating the components for a period of 10 minutes. The suspension formed from this high intensity mixing remained a homogeneous gel indefinitely in the aromatic solvents. Heating, shaking by hand, and agitating via dispermat were found to be inferior methods for dispersing organoclays. These methods resulted in phase separation of the clay and the solvent within a period of hours. The upper limit of clay loading with respect to toluene was determined to be 4 – 5 wt.-%. At this concentration, the suspension was well-suited for ultrasonic agitation, thus enabling a more efficient dispersion. These results led to the future parameters of this project to include a 10 minute period of ultrasonic agitation at a maximum 3 wt.-% organoclay in toluene.

3.2.3 Developing Polymerization on As-received L-lactide

Polymerizations in vials were conducted testing the effects of clay loading (1 %, 5 %, and 10 %) and absence of Sn(Oct)₂ catalyst versus the synthesis of pristine PLLA with catalyst present. These experiments used L-lactide as-received with no means of purification. As was expected, without the metal catalyst present in the reaction, the polymerization of L-lactide did not occur. All products were darker than desired. Sample properties prepared this way were not ideal based on simple qualitative assessment.

Catalyst concentration studies at [monomer]₀/[Sn] molar ratio of 40,000, 4,000, 1600, and 800 were done using 5 % organoclay (1) in as-received L-lactide to get an idea of its effect on molecular weight and properties of PLLA-nanocomposites. After several polymerizations took place, the importance of purifying the monomer was made known via consultations with NatureWorks[®] LLC. This was confirmed by GPC, which showed molecular weights much lower than expected, which meant that too many initiators were present in the as-received monomer.

3.2.4 *In situ* Polymerization of PLLA from Purified L-lactide

At this time, L-lactide was purified as described in Section (2.1) with one rinse (p-1-L-lactide). The catalyst concentrations mentioned in the previous section were compared with pristine PLLA. The molecular weights obtained (GPC) were far lower than expected for polymerizations of pure monomer with no clay/initiators present. A trend was established which showed that as catalyst concentration increased, the molecular weight did so concomitantly, as shown on the next page in Figure 8.

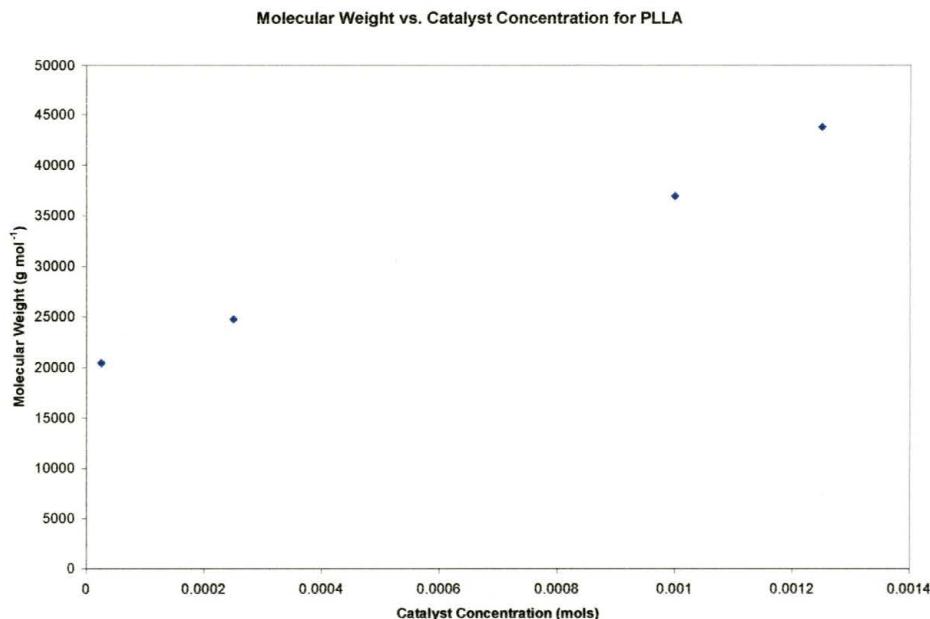


Figure 8. Plot of Molecular Weight vs. $\text{Sn}(\text{Oct})_2$ Catalyst Concentration for PLLA.

This trend is not well understood, since the molecular weight of the polymer is directly correlated to the amount of hydroxide initiators present and not the concentration of the catalyst. Also, from these experiments, it was demonstrated that a higher viscosity during reaction and difficulty to separate product from glassware was indicative of higher molecular weight polymers. The molecular weights were inferior to those of commercially available PLLA samples. This was thought to be a result of storing purified reagents in air-free flasks in laboratory atmosphere for several weeks. Over time, air would enter the flasks and contaminate the reagents. NatureWorks® PLLA was determined to have a M_w of 96,000 g mol⁻¹.

3.2.5 Polymerization of PLLA-MMT from Purified L-lactide

The four vial polymerizations utilizing clay at 4.3 % were performed using p-1-L-lactide. Reactions with a mole ratio of monomer to catalyst of 40,000 and 4,000 polymerized, but turned completely black after 8 h. The reactions with monomer: catalyst of 1600: 1 and 800: 1 showed less color in the final polymer composite. All four products are shown below in Figure 9.



Figure 9. 4.3 % Organoclay (1) Loaded PLLA-nanocomposite. $[\text{monomer}]_0/[\text{Sn}]$ molar ratio of (a) 40,000, (b) 4,000, (c) 1,600, (d) 800.

When organoclays were present in the reactions, increasing the catalyst concentration would give a more favored colorless product. This could be attributed to the quicker polymerization of the more concentrated catalyst reactions leaving less time for decomposition of the monomer at elevated temperatures. Also, if catalyst molecules were having difficulty intercalating into the clay galleries, where initiators are located, increasing the concentration would allow for a more likely interaction of catalyst to initiator. Since clay loading was held constant in these experiments, a higher concentration of catalyst is preferred from a qualitative standpoint. A monomer to catalyst ratio of 800: 1 was utilized in this synthesis after these comparisons were made.

3.2.6 Macroscale Polymerizations of PLLA and PLLA-MMT

The reactions conducted in 250 ml three-necked flasks gave very dark, brittle products which were not ideal. Monomer used in macroscale reactions was p-1-L-lactide. The final product seemed to have a low molecular weight based on its brittle character. It is known that polymers have to be of a certain molecular weight before they have useful properties. When molecular weights are too low, the attractive forces between molecules are not strong enough to give rise to the molecular cohesion and resultant mechanical strength. At this time, the dark color was assumed to be a direct result of air remaining in the system leading to oxidation of the polymer composite. Any attempts to produce films for mechanical studies proved useless, since the material would fracture upon removal from molds due to its brittle state. At a $[\text{monomer}]_0 / [\text{Sn}]$ molar ratio of 800, a low M_w of approximately $25,000 \text{ g mol}^{-1}$ was obtained. The reason for getting such low molecular weights and mechanical properties was not understood. At this point, the purity of the monomer, reaction time, and catalyst concentration were considered in an attempt to solving molecular weight issues. The next set of reactions were performed free of organoclays to lower the amount of variables which could be causing problems in the polymerization of PLLA.

3.2.7 Polymerization of PLLA at Two Hour Intervals (2 Rinses)

In the present organoclay-free reactions, polymerizations were quenched every 2 hours starting at 2 h and ending at 10 h after temperature reached 180°C . The monomer used in this case was purified with 2 rinses (p-2-L-lactide). Alongside these reactions was a polymerization which used p-1-L-lactide as the monomer and was removed after

8 h. Molecular weights were determined for the 8h and 10 h reactions that started with p-2-L-lactide monomer and 8 h polymerization of p-1-L-lactide. All reactions in this series were at a $[\text{monomer}]_0 / [\text{Sn}]$ molar ratio of 40,000. Both reactions using p-2-L-lactide had a M_w of approximately 200,000 g mol⁻¹, which revealed that 8 h was a sufficient time for polymerization to occur. The reaction with p-1-L-lactide gave a M_w of approximately 160,000 g mol⁻¹. By rinsing the recrystallized product more than once, less hydroxide-containing species or initiators remained in the starting material, giving rise to higher molecular weight products.

3.2.8 Catalyst Concentration Study at 3 % Organoclay Loading

A series of reactions were tested to determine the optimal catalyst concentration for a polymerization of PLLA-nanocomposite similar to those described in Section 3.2.5. However, the L-lactide used in this study was purified with 2 rinses. Organoclay (1) was added to the reaction at a lower concentration of 3 wt.-% in monomer. For these reactions, $[\text{monomer}]_0 / [\text{Sn}]$ molar ratios of 40,000, 4,000, 2,000, 1,333, 1,000, and 800 were studied. The reactions containing the two lowest catalyst concentrations showed no signs of polymerization. Once cooled to room temperature, the final product in these two cases had a syrupy consistency. All other products resembled conventional polymer nanocomposites. In the case of the other polymerizations, as catalyst concentration increased, the degree of color darkening decreased concurrently up to monomer to catalyst ratio of 1000. Molecular weights were not obtained for these products due to problems with the GPC. However, the differences in the products can be seen in Figure 10.

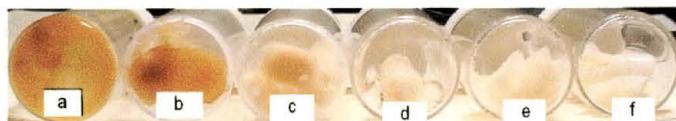


Figure 10. 3 % Organoclay (1) Loaded PLLA-nanocomposite. $[\text{monomer}]_0 / [\text{Sn}]$ molar ratio of (a) 40,000, (b) 4,000, (c) 2,000, (d) 1,333, (e) 1,000, (f) 800.

After this set of polymerizations were conducted, a $[\text{monomer}]_0 / [\text{Sn}]$ molar ratio of 1,000 was chosen especially in the case of reactions utilizing organoclays.

3.2.9 Effect of Organoclay Loading on PLLA-nanocomposite

Polymerizations were conducted at 1, 2, 3, 4, and 5 wt.-% organoclay loadings. The amount of organoclay present in these reactions was directly related to the color of the final product. In this case, the color difference between each sample was very subtle and is to be expected for an increase in clay loading. Molecular weights (M_w) were determined to be $64,000 \text{ g mol}^{-1}$ and $37,000 \text{ g mol}^{-1}$ for 1 % and 5 % organoclay (1) – loaded PLLA-MMT, respectively. In an experiment described later, a 4 wt.-% organoclay-nanocomposite was synthesized. A plot of M_w with respect to organoclay loading is shown on the next page in Figure 11.

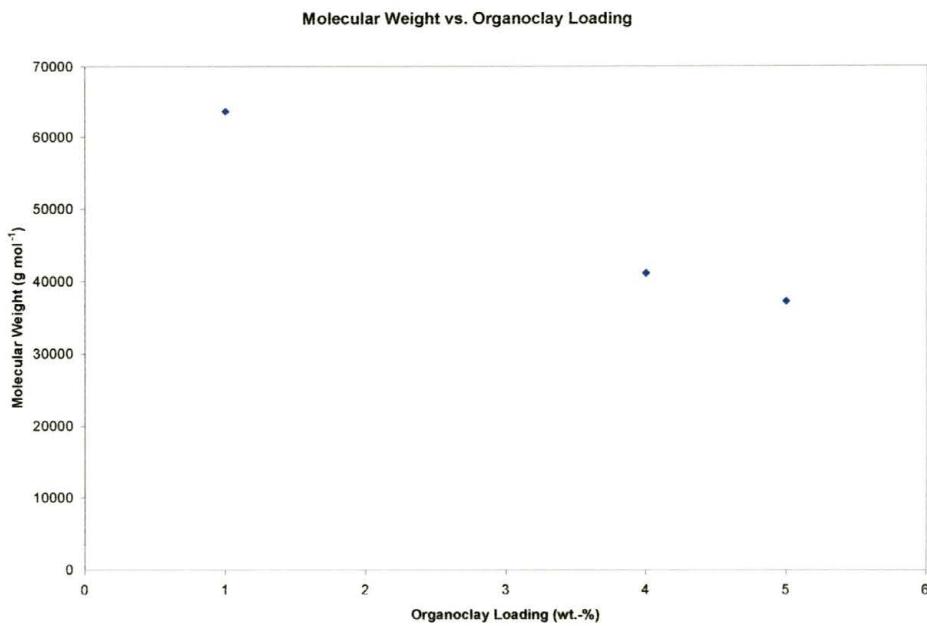


Figure 11. Plot of Molecular Weight Dependency on Organoclay Loading.

A decrease in molecular weight with increase in organoclay is expected if the organoclay is functionalized with hydroxyl-terminated alkylammonium initiators.

3.3 Water on Na⁺: A Possible Culprit for Low Molecular Weights

After numerous failed attempts at synthesizing PLLA-nanocomposites with molecular weights between 75,000 g mol⁻¹ to 100,000 g mol⁻¹, the possibility that water associated with Na⁺ ions may have been hydrolyzing the L-lactide monomer was suggested. Na⁺ ions are displaced from the surface of the clay and interact with Cl⁻ counterions associated with the quaternary ammonium compounds. When L-lactide undergoes hydrolysis, two moles of lactic acid are formed, which can act as initiators, thus lowering the molecular weight of the polymer. This was the reasoning behind excessively washing the 2M2HT/MT2EtOH-modified-MMT with deionized water until a simple AgNO₃ test would reveal the absence of Cl⁻ ions, or indirectly Na⁺ ions.

Polymerizations with washed organoclay were done at 1 % and 5 % organoclay (2) loading. The molecular weights (M_w) of the washed-organoclay polymerizations were determined to be 67,000 g mol⁻¹ and 53,000 g mol⁻¹ for 1 % and 5 % organoclay-loaded PLLA-MMT, respectively. There was an overall increase in molecular weight by excessively washing the organoclays prior to using them for polymerizations, but the increase was not very significant, especially at lower clay loadings. From these experiments, the inorganic salts were removed from the list of potential culprits lowering the molecular weight of PLLA-MMT.

3.4 Possibility of Edge Hydroxides Lowering Molecular Weight

After eliminating the possibility that water from Na⁺ ions was playing a negative role in the polymerization, the hydroxyl-terminated clay edges were then considered. The silane-coupling agent, phenyl triethoxy silane, was added to the organoclay in order to react with any –OH groups on the edges of the clay plates that could possibly contribute to the initiation of extra polymer chains, thus lowering the molecular weight of the final product. A reaction with 4 % silane-treated organoclay was carried out and resulted in a PLLA-MMT with M_w of 55,000 g mol⁻¹. This molecular weight was logical since the amount of hydroxyl-terminated alkylammoniums was greater than the 1 % organoclay-loaded sample but less than the amount on the 5 % sample. There was a noticeable increase in the molecular weight from 41,000 g mol⁻¹ to 55,000 g mol⁻¹ after the organoclay was treated with a silane coupling agent. Treating the hydroxyl-containing edges of the clay plates did not change the molecular weight of the product sufficiently to account for the lowered molecular weights. Also, samples were not run in

triplicate to determine the error of the molecular weight. As stated previously, molecular weights of $70,000 \text{ g mol}^{-1}$ or greater are desired for PLLA or PLLA-MMT.

3.5 Attempt to Increase Molecular Weight with Dimethyl Terephthalate

A polymerization was performed in which dimethyl terephthalate was added prior to the termination of the reaction. This experiment was performed in order to see if the molecular weight could be increased by linking two polymer chains to one terephthalate molecule. If the addition was employed toward the end of the reaction, the molecular weight would theoretically be increased significantly. Unfortunately, for a 4 wt.-% organoclay loaded polymerization, the M_w only increased by about $7,000 \text{ g mol}^{-1}$. Since the polymerization with dimethyl terephthalate was allowed to react for a slightly longer period of time, the increase was insignificant. Figure 12 is a plot of M_w versus organoclay loading including the addition of dimethyl terephthalate in reference to previous loading data.

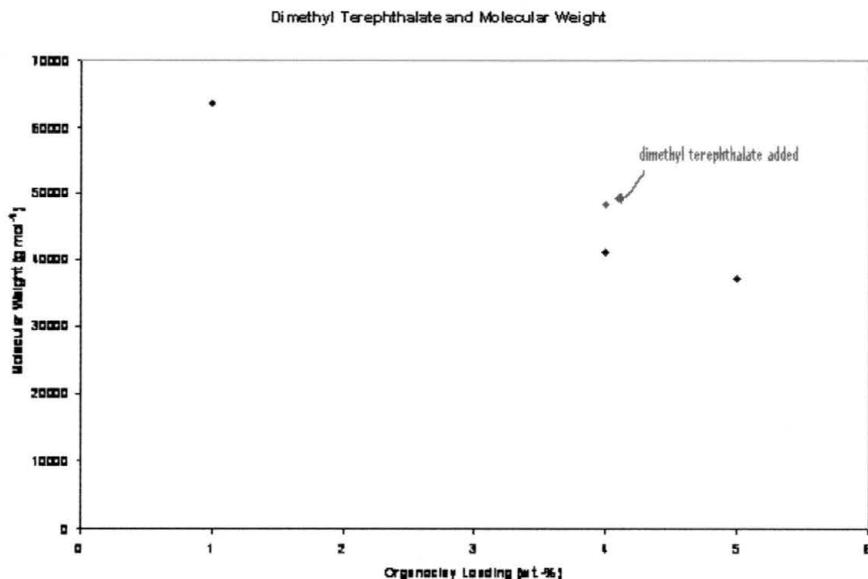


Figure 12. Plot of Molecular Weight vs. Organoclay Loading Including Addition of Dimethyl Terephthalate.

3.6 Pristine Reaction for Targeting High Molecular Weights Products

After attempting to increase the molecular weight of the PLLA-MMT by modifying the organoclay, a polymerization in the absence of organoclay was conducted. This reaction would reveal if the organoclay was causing this major drop in molecular weight of PLLA-MMT. After analyzing the product by GPC, the molecular weight was determined to be $75,000 \text{ g mol}^{-1}$. This molecular weight is unsatisfactory for a pristine run, since the value obtained is in the range of desired molecular weights of polymers initiated from organically-modified layered-silicates. In other words, there are enough initiators present inherently in reagents to bring the molecular weight to the desired range, leaving no room for additional initiators coming from layered-silicates. This study revealed that either the reagents (i.e., L-lactide, toluene, $\text{Sn}(\text{Oct})_2$ solution) or the experimental procedure were not sufficient for the polymerization at hand.

3.7 Reagent Purity and Ultrasonic Agitation

A pristine synthesis was performed in which every parameter was left unchanged, except that ultrasonic agitation was removed from the procedure. This experiment would determine whether the extra initiators were a direct result of contamination during ultrasonic agitation or reagent purity. The reagents are the most vulnerable during agitation, because this is the only moment when any of the reagents are exposed to laboratory atmosphere. The final product had a M_w of $97,000 \text{ g mol}^{-1}$. This molecular weight, although improved, was indicative of an unacceptable amount of inherent initiators present in the reagents. The increase in molecular weight can be attributed to

the fact that the reagents were taken from the dry box directly to the hood with minimal exposure to laboratory atmosphere. This would minimize contamination, thus lowering the amount of hydrolysis in the reagents. New means of purification, drying, and storing were determined to be invaluable to the polymerization of PLLA-MMT.

3.8 High Molecular Weight PLLA with Purest Reagents

For this polymerization and those following, all reagents were dried and purified to the best of our efforts, then taken directly to the dry box for storage. Even though purification was found to be a critical part of this polymerization, storing in laboratory atmosphere defeated the purpose of recrystallization, unless reagents were used hastily after purification. Also, anhydrous solvents were obtained by distilling over sodium instead of from commercially available anhydrous solvent providers. This decision was made after realizing that air/moisture was permeating the seal and wetting the solvents over time. The $\text{Sn}(\text{Oct})_2$ catalyst was vacuum distilled in an attempt to remove acidic impurities, and this new catalyst was used in all remaining experiments.

Ultrasonic agitation was performed with argon flowing over reagents, in order to minimize the likelihood of exposure to air. Every step of this polymerization was carried out as before. After purifying the reagents to this extreme, poly(L-lactide) with a M_w of approximately $320,000 \text{ g mol}^{-1}$ was produced. This reaction showed that purification measures and storage were adequate for polymerizations of high molecular weight polymers. From these results, there was no apparent reason why PLLA-MMT of at least $70,000 \text{ g mol}^{-1}$ could not be achieved.

3.9 Testing Pure Reagents with 2M2HT/MT2EtOH-modified Clay

After successfully polymerizing high molecular weight poly(L-lactide), a polymerization with 5 wt.-% organoclay (2) was run. At the MT2EtOH concentration of organoclay (2), a loading slightly greater than 5 % should give a molecular weight comparable to commercial PLLA. Surprisingly, the M_w obtained for this reaction was a low $50,000 \text{ g mol}^{-1}$. After this result, other types of quaternary ammoniums were studied for their effect on molecular weight and color of PLLA-MMT.

3.10 Reaction with Hydroxyl-free Alkylammonium-modified-MMT

Cloisite® 20A (95 mequiv 2M2HT/100g clay) was tested as an organoclay in a polymerization. It has no hydroxyl-terminated quaternary ammoniums, so theoretically it should not lower the molecular weight of the final polymer. After following all of the same procedures as before, a polymer with a M_w of only $22,000 \text{ g mol}^{-1}$ was obtained. The final product was also very dark in color, which suggested that reagents were degrading at the polymerization conditions in use. Using a hydroxyl-free (i.e., initiator-free) organoclay as the inorganic filler and getting an extremely low molecular weight suggests that the specific quaternary ammonium used is adversely participating in the synthesis of PLLA-MMT. 2M2HT was the major constituent of the organoclay which was used for the majority of this study, so this explains why PLLA-MMTs would darken over the course of the polymerization.

3.11 PLLA-MMT with New Organoclay

Polymerizations were run at 5 wt.-% organoclay (4) and (5). These organoclays were modified with 85.5 meq 2M2HT/100g clay and 9.5 meq MT2EtOH/100g clay. Organoclays (4) and (5) were prepared with 5 wt.-% and 2.5 wt.-% silane coupling agent, respectively. These were the final attempts at polymerizing PLLA-MMT using 2M2HT as a diluent modifier (i.e., does not initiate polymerization). Final products were very dark in color and were thus not reliable products for commercial use.

3.12 Polymerization of PLLA with Free Quaternary Ammoniums

A study was carried out in which 2M2HT and MT2EtOH were added as reagents. There was no clay used in this study; just the quaternary ammonium surfactants that would normally be ion-exchanged onto layered-silicates. This was done in order to see if the undesired color from past polymerizations was coming from the surfactants which may have been removed from within the clay galleries during the synthesis of PLLA-MMT. After reacting for 8 hours at 180°C, the final polymer became darker and more brittle than any other product we had synthesized before. Unfortunately, molecular weights could not be achieved from the GPC for this product. From this observation, it was demonstrated that 2M2HT was a poor choice of a quaternary ammonium for the polymerization of PLLA-MMT.

3.13 PLLA-MMT with MT2EtOH-modified Organoclay

PLLA-MMT was synthesized at 1 wt.-% Cloisite® 30B. This organoclay is modified at 90 meq MT2EtOH/100g clay. Without substituting some MT2EtOH

surfactants with hydroxyl-free quaternary ammoniums, the molecular weight was expected to be low. This study was done in order to monitor the color of the PLLA-MMT throughout the course of the reaction. The final product showed very little color, and MT2EtOH was determined to be a satisfactory surfactant for this reaction. Molecular weights could not be obtained from GPC at this time. Also, XRD revealed an exfoliated product by the absence of peak order from clay delamination, as shown below in Figure 13.

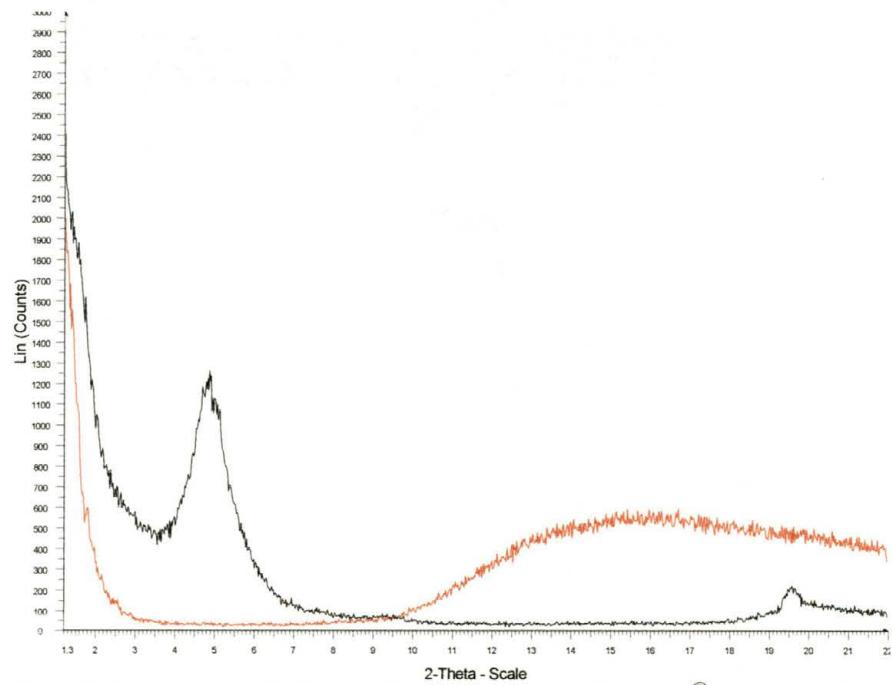


Figure 13. XRD Scans of PLLA-MMT with 1 % Cloisite® 30B (Red) and Pure Cloisite® 30B (Black).

Since the organoclay used in this experiment was exclusively modified with MT2EtOH, the high grafting density would be expected to aid in the exfoliation of the clay plates.

3.14 PLLA-MMT with TEQ-modified Organoclay

PLLA-MMT was synthesized at 1 wt.-% TEQ-modified organoclay. At 95 meq TEQ/100 g clay, this hydroxyl-terminated quaternary ammonium was expected to result in a low molecular weight product since no diluent (hydroxyl-free) surfactants were employed. The TEQ-modified organoclay would however enable a higher clay loading than the MT2EtOH-modified organoclay since it is monosubstituted with a hydroxyl group rather than disubstituted. There was also no order shown in the XRD scan. This suggested that the PLLA-MMT polymerized from TEQ-modified organoclay was exfoliated. An ideal, low color content PLLA-MMT was produced when TEQ-modified organoclay was used as the initiator. Molecular weight was not obtained from the GPC at this time.

3.15 Substitution of Various Quaternary Ammoniums for 2M2HT

After performing the reactions utilizing 2M2HT-modified organoclay, discussed in previous sections, it was decided that octadecylammonium may be a better candidate for a hydroxyl-free quaternary ammonium in the polymerization of PLLA-MMT. A polymerization was performed at 5 wt.-% octadecylammonium-modified organoclay. Even at such a high clay loading, there was little color in the final product which made octadecylammonium a good substitute for 2M2HT. The X-ray diffraction pattern for this product also showed complete exfoliation of clay sheets in the polymer matrix. This could be due to the clay galleries and the prepolymer being more miscible than in the case of 2M2HT.

Cloisite® 10A (2MBHT-modified-MMT) and DEQ-modified-MMT were also examined as possible hydroxyl-free quaternary ammoniums, but resulted in very dark final products, which were not ideal, since it was proposed that the dark color of the product was correlated to the molecular weight issues.

3.16 PLLA-MMT from TEQ/ODA-modified Organoclay

Once it was determined that TEQ and ODA gave lightly colored PLLA-MMT products, a polymerization was conducted using an organoclay which was modified with 76 meq ODA/100g clay and 19 meq TEQ/100g clay. These reactions were conducted at 5 wt.-% organoclay loading for 2 h and 8 h durations. The final products had the lowest color character from all of the polymerizations. Unfortunately, the resultant PLLA-MMT was still lacking in molecular weight, at approximately $21,000 \text{ g mol}^{-1}$. Although the molecular weight of this nanocomposite was lower than desired, further studies will be conducted using TEQ, MT2EtOH, and octadecylammonium as surfactants for montmorillonite.

CHAPTER 4

CONCLUSIONS

Initially, we did not expect the reagents, specifically the monomer, to be so sensitive to laboratory atmosphere. After a series of reactions were performed, the importance of storing reagents in a dry box was determined. In laboratory atmosphere, the hydrolysis of crystalline L-lactide to a viscous hygroscopic lactic acid solution could be observed over a period of days to weeks. Commercially, lactic acid is added as a source for hydroxyls in order to reduce the molecular weight to the desired range. Therefore, the addition of an initiator-containing organoclay in this study was excessive. Also, the importance of excessively rinsing the purified monomer after recrystallization was not realized until several polymerizations were conducted. Ideally, all reagents would be prepared in a dry box, and seeing that the polymerization is ring-opening, reactions would be performed in sealed vials under a hood. However, in this study, toluene was utilized as an aid to dispersing clay platelets into the PLLA matrix. At polymerization temperatures, toluene was evaporated from the reaction and collected in a catch flask. This setup along with ultrasonic agitation procedures increased the likelihood of exposure to air/moisture from the laboratory atmosphere. Although great care was taken in order to remove impurities from the reagents, it is likely that significant levels remained in the Sn(Oct)₂ catalyst solution. It is believed that contaminants in the catalyst and monomer are the true initiators in L-lactide polymerizations.³⁹ A more

effective high-vacuum distillation procedure for the purification of the Sn(Oct)₂ may be required along with analysis under ¹H NMR for acidic impurities.⁴⁰ There is no question that exhaustive purification is critical for the polymerization of high molecular weight PLLA.

For GPC preparation, all samples were dissolved prior to being tested. High molar mass fractions may have been filtered off resulting in a large reduction in M_w and a small increase in M_n. It may be worthwhile to first eliminate the clay from the PLLA chains via cationic exchange reaction with LiCl prior to molecular weight determination. Paul et al. prepared samples for GPC analysis using this technique.¹⁷

After letting PLLA samples sit in laboratory atmosphere for months, condensate was observable on the walls of the vials. Hartmann et al. found that fragment onset for PLLA is at 2.0 years and biodegradation is complete at 3.1 years at 25°C and 80 % relative humidity.² These conditions are common in our laboratory, so analysis of samples should be performed soon after PLLA synthesis, especially since introducing inorganic fillers into polymer systems has been shown to significantly enhance biodegradation.⁴¹

For PLLA-MMT synthesized from hydroxyl-containing organoclays, a trend was established showing that as clay loading increased, molecular weight decreased. This is to be expected since adding more organoclay adds more initiators to the polymerization. A direct correlation between catalyst concentration and molecular weight was determined for this synthesis. It was determined that an excess amount of Sn(Oct)₂ catalyst was required when organoclays were used as initiating species. This fact may be due to the diminished possibility of catalyst reaching initiator considering the high aspect ratio of

the clay platelets. If there was only a limited degree of intercalation of prepolymer into the clay galleries, there is a possibility that the initiating/catalytic properties of the tin(II) alkoxide or hydroxide went unutilized. From these studies, it was confirmed that the optimal catalyst concentration for a pristine polymerization of PLLA (180°C, 8 h) was [monomer]₀/[Sn] molar ratio of 40,000. Also, the optimal [monomer]₀/[Sn] molar ratio for a polymerization of PLLA-MMT under the same conditions was determined to be ~ 890 or approximately 45 times that of the pristine run. When reactions were carried out at concentrations higher than those mentioned, the polymer chains would reach a maximum length before the 8 h period was complete. The final product would then suffer from serious discoloration after this time, which is thought to be a sign of thermal decomposition of quaternary ammoniums.

XRD analysis revealed that several organoclays that were functionalized with only one quaternary ammonium gave better delamination or exfoliation in this synthesis. This phenomenon was most likely due to the high grafting density in the case of monofunctionalized organoclays. Using quaternary ammoniums that contain one –OH group (e.g., TEQ) allows for a higher clay loading than if the surfactant is bifunctional (e.g., MT2EtOH). This would permit more room for enhancement of nanocomposite properties by not lowering molecular weight with an excess of initiators. On the other hand, by using bifunctional quaternary ammoniums, there would be a higher chance that exfoliation would occur due to the higher density of growing chains on the surface of the clay plates. DSC and Dynamic Mechanical Analysis (DMA) did not provide valuable data since ideal PLLA-MMT nanocomposites were not synthesized in this project.

PLLA nanocomposites with significant enhancement in mechanical and thermal properties have not yet been synthesized. In 2003, Paul et al. reported exfoliated polylactide/clay nanocomposites by *in situ* polymerization, but molecular weights (M_n) of merely 14,400 g mol⁻¹ were obtained.¹⁷ Although the PLLA-nanocomposites with improved thermal properties, e.g., HDT, were not synthesized in the present study, many issues were elucidated, bringing the ultimate goal within much closer proximity.

It has been established that catalyst concentration, polymerization time, and temperature greatly influence the polymer yield and molecular weight, so more fine-tuning of parameters would be beneficial to the study of PLLA-MMT. A more detailed analysis is needed for explaining discoloration mechanisms. In future work, surfactants will be adjusted in order to achieve the greatest improvement in properties of PLLA-MMT.

Studies have shown that molecular weight of PLLA decreased with increasing polymerization temperatures.⁴ Future studies will attempt to increase molecular weights of nanocomposites and lessen the amount of degradation by investigating polymerizations at lowered reaction temperatures. Lastly, samples will be doped with small amounts of NaCl to confirm that the Na⁺ was not contributing initiators.

APPENDICES

APPENDIX 1

Molecular Weights (GPC) and Comments on Products

Polymer/ Nanocomposite	M_n	M_w	Comments
1. NatureWorks® PLLA	50,721	95,850	Commercial sample
2. Pristine PLLA (40,000 mols monomer: 1 mol catalyst)	12,477	20,438	Low viscosity melt, easy to separate from glassware
3. Pristine PLLA (4,000 mols monomer: 1 mol catalyst)	13,834	24,759	Medium viscosity melt, easy to separate from glassware
4. Pristine PLLA (1,600 mols monomer: 1 mol catalyst)	17,268	36,920	High viscosity melt, difficult to separate from glassware
5. Pristine PLLA (800 mols monomer: 1 mol catalyst)	17,954	43,806	High viscosity melt, difficult to separate from glassware
6. 4.28 wt.-% organoclay (1) in PLLA (40 g batch)	6,003	14,228	Dark, brittle product
7. 3 wt.-% organoclay (1) in PLLA (50 g batch)	7,964	16,493	Better color, brittle
8. Pristine PLLA (50 g batch) impure monomer	13,548	22,951	Good color – slightly yellowed
9. Pristine PLLA – 8 h (5 g batch) Pure- 2 wash	130,915	200,743	Good color, Difficult to separate from glassware
10. Pristine PLLA – 10 h (5 g batch) Pure- 2 wash	135,212	195,164	Good color, Difficult to separate from glassware
11. Pristine PLLA (5 g batch) Pure- 1 wash (8 h)	97,810	162,159	Good color, Difficult to separate from glassware

12. 3 wt.-% organoclay (1) in PLLA (5 g batch) (monomer: catalyst varied from 40,000:1 to 800:1) Pure- 2 wash	n/a	n/a	As the catalyst concentration was increased, the amount of color in the product was decreased The reaction with 40,000: 1 monomer to catalyst ratio did not polymerize determined by lack of viscosity 1,000: 1 gave the best properties Catalyst concentration must be increased when organoclay is used
13. 1 % organoclay (1) in PLLA (5 g batch) (1,000 mols monomer: 1 mol catalyst) Pure- 2 wash	29,318	63,637	Became viscous after ½ h reaction time
14. 5 % organoclay (1) in PLLA (5 g batch) (1,000 mols monomer: 1 mol catalyst) Pure- 2 wash	20,270	37,200	Became viscous after ½ h reaction time
15. 1 % organoclay (2) in PLLA (10 g batch) (1,000 mols monomer: 1 mol catalyst) Pure- 2 wash	32,862	67,033	Good color, Difficult to separate from glassware
16. 5 % organoclay (2) in PLLA (10 g batch) (1,000 mols monomer: 1 mol catalyst) Pure- 2 wash	26,719	53,119	
17. 4 % organoclay (2) in PLLA (5 g batch) – no dimethyl terephthalate added	18,746	41,115	
18. 4 % organoclay (2) in PLLA (5 g batch) – dimethyl terephthalate added	22,954	48,477	Product degradation

19. 4 % organoclay (3) in PLLA (5 g batch)	31,969	55,407	Organoclay did not disperse as well in toluene Product degradation
20. Pristine PLLA (5 g batch) (all reagents/procedures kept constant except organoclay was not added)	37,390	75,404	
21. Pristine PLLA (5 g batch) (NO ultrasonic agitation)	45,237	96,511	Solution became viscous immediately once reaction conditions were met
22. Pristine PLLA (5 g batch) (new, drier/purer reagents used)	192,162	321,754	
23. 5 % organoclay (2) in PLLA (5 g batch) (new, drier/purer reagents used)	31,278	49,807	
24. 5 % Cloisite® 20A in PLLA (5 g batch) (new, drier/purer reagents used)	12,306	21,979	
25. PLLA with free quaternary ammoniums (no clay)	4,320	7,601	Very brittle product Non-viscous during reaction Very dark final color Quats cause degradation with catalyst at 180C when not exchanged on clay surface Slight amine smell
26. 1 % Cloisite® 30B in PLLA	10,475	20,279	GPC graph did not have a good baseline
27. 1 % organoclay (6) in PLLA	40,596	63,170	GPC graph did not have a good baseline Good color Darkened slowly over time, which is what happens to pristine PLLA when excess catalyst is used and kept at 180°C longer than needed

28. 5 % organoclay (7) in PLLA	n/a	n/a	Good color MW probably low Properties probably not good since polymerization did not occur from clay plates
29. 5 % Cloisite® 10A in PLLA	n/a	n/a	Very brittle product, low MW Easily removed from reaction flask
30. 5 % organoclay (9) in PLLA (2 h)	13,945	22,586	Very good color for high clay loading
31. 5 % organoclay (9) in PLLA (8 h)	11,697	20,742	Very good color for high clay loading

APPENDIX 2

XRD/TGA Values for Reagents/Products

Polymer/ Nanocomposite	d-spacing (Å)	Intensity (Counts)	Decomposition Temperature (TGA) (°C)
1. p-1-L-lactide	n/a	n/a	209 (onset ~ 125)
2. Cloisite® Na ⁺	11.7, 4.5	430, 300	
3. 2M2HT	n/a	n/a	216 (15 % loss) 358 (85 % loss)
4. MT2EtOH	n/a	n/a	246 (30 % loss) 306 (70 % loss)
5. Organoclay (1)	49.2, 26.0, 12.9, 4.5	1550, 3200, 550, 250	262
6. Organoclay (1) – dispersed	25.9, 12.4, 4.5	900, 150, 150	n/a
7. Organoclay (9)	n/a	n/a	348 (7 % loss) 387 (8 % loss)
8. 1 % organoclay (1) in PLLA (no agitation)	n/a	200	n/a
9. 1 % organoclay (1) in PLLA	32.3	30	263
10. 5 % organoclay (1) in PLLA	n/a	100	263
11. 1 % organoclay (2) in PLLA	n/a	n/a	295
12. 4 % organoclay (3) in PLLA	35.5, 17.3	295, 60	n/a
13. 5 % organoclay (2) in PLLA (new drier/purer reagents used)	34.8, 17.4	525, 90	304
14. 5 % organoclay (4) in PLLA (new drier/purer reagents used)	74.9, 29.2, 16.0	40, 35, 35	314

15. 1 % Cloisite® 30B in PLLA	no peaks	no peaks	299
16. 1 % organoclay (6) in PLLA (new drier/purer reagents used)	no peaks	no peaks	289
17. 5 % organoclay (7) in PLLA (new drier/purer reagents used)	no peaks	no peaks	315
18. 5 % organoclay (9) in PLLA (new drier/purer reagents used)	60.5, 35.9	875, 350	339 (2 h) 337 (8 h)

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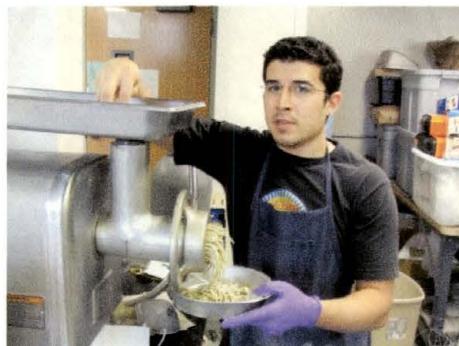
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